AR201-13405A

HIGH PRODUCTION VOLUME (HPV)

CHEMICAL CHALLENGE PROGRAM

TEST PLAN

For

CHLOROACETYL CHLORIDE

Prepared by:

The Dow Chemical Company

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EXECUTIVE SUMMARY

The Dow Chemical Company hereby submits for review and public comment the test plan for chloroacetyl chloride (CAC), which we have classified as a closed-system intermediate, under the Environmental Protection Agency's (EPA) High Production Volume (HPV) Chemical Challenge Program. It is the intent of The Dow Chemical Company to use existing data and scientific judgment and analyses to adequately characterize the SIDS (Screening Information Data Set) human health, environmental fate and effects, and physicochemical endpoints for this chemical.

Please note that we are aware that there is another producer and an importer of CAC in the United States. We have been in contact with each of these companies to determine if they were interested in joining with Dow in our commitment to the HPV Chemical Challenge Program. Unfortunately, each of these companies declined our invitation to participate with us in making this HPV commitment. Further, we asked them to assess whether their production, handling, and use of CAC would fulfill the criteria outlined by EPA for a closed-system intermediate. Both of these companies confirmed that their production, handling and use of CAC satisfied the Agency's criteria for a closed-system intermediate.

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I. INTRODUCTION

The Dow Chemical Company has voluntarily committed to develop and/or summarize screening level human health effects, environmental effects and fate, and physicochemical test data for chloroacetyl chloride under the Environmental Protection Agency's (EPA's) High Production Volume (HPV) Challenge Program.

This plan identifies the chemical and its CAS number, identifies existing data of adequate quality for the chemical, and provides justification for why additional data does not need to be generated for the chemical under the Program.

II. DESCRIPTION OF CHLOROACETYL CHLORIDE

A. The Chemical

Chloroacetyl chloride (CAC) (CAS No. 79-04-9), a compound manufactured from vinylidene chloride, is used as an intermediate, primarily in the production of agricultural and pharmaceutical compounds. It is a colorless or slightly yellow liquid at room temperature. It has a strong, pungent odor similar to that of hydrochloric acid, which serves as a fairly reliable warning of its presence. However, even at increasing concentrations, the vapors can dull the sense of smell and make detection difficult.

Table 1. Chemical/physical properties Chloroacetyl Chloride

Chemical Abstract Number	79-04-9
Molecular formula	***$CH_2ClOCCl$***
Molecular weight	***112.9***
Physical State	***Colorless to Light yellow liquid***
Freezing Point	**-7.8°F/-22°C**
Boiling point	**223°F/106°F**
Vapor pressure	**33.3 hPa @ 25°C**
Water Solubility	**Reacts to decompose**
Specific Gravity	**1.41 (25/25°C)**

The health hazards to humans can be summarized as follows:
Eyes: Liquid CAC and its vapors may irritate or damage the cornea, causing permanently impaired vision or blindness.
Skin: A single exposure of a few minutes can cause severe burns and may result in rapid absorption of lethal amounts.
Ingestion: There is little likelihood that ingestion will occur in routine industrial

applications. Nevertheless, small amounts may cause burns of the mouth and throat. Ingestion of large amounts can be fatal.
Inhalation: Excessive exposure to vapors may irritate upper respiratory tract, nasal passages and lungs. Pre-existing lung conditions may be aggravated.

There are a limited number of environmental toxicity and fate studies that exist for the chemical itself due to the reactivity of CAC with water. However, since the material hydrolyzes **within minutes** in water to form hydrochloric acid and chloroacetic acid, the material is believed to be analagous to chloroacetic acid, particularly in terms of its environmental effects. Therefore, many of the environmental studies referenced pertain to chloroacetic acid, and are referenced as such below and in the attached Robust Summaries.

III. TEST PLAN RATIONALE

A. Classification of the Chemical as a Closed-System Intermediate

1. Requirements

Classification of chloroacetyl chloride as a closed-system intermediate under the EPA HPV program is dependent upon a number of criteria outlined by EPA. The Dow Chemical Company asserts that chloroacetyl chloride should be regarded as a closed-system intermediate, based on satisfaction of these criteria. In the following paragraphs, information is provided on the extremely limited potential for exposure during manufacturing, transport, and processing.

2. Satisfaction of Requirements

a. Review of Manufacture / Transport / Consumption:
Chloroacetyl Chloride (CAC) is produced in a single facility within The Dow Chemical Company's Michigan Operations Site located in Midland, Michigan. It has been manufactured since 1972. CAC is manufactured in a closed system from vinylidene chloride. The majority of the CAC is consumed within the same facility in the production of other chlorinated derivatives. A very small percentage is sold to off-site customers, who also utilize CAC as an intermediate. After the CAC is produced, it is placed in one of several storage tanks, which are all vented to a scrubber, and located in a dike area. For internal consumption, CAC is transferred to the reactors as needed via pipeline. For off-site consumption, the CAC is loaded, via a closed system with a vapor return line, into isocontainers. The isocontainers are specially designed tanks surrounded by a frame that allow greater portability and also minimizes the potential for damage to occur during transit. The isocontainers are equipped with dry-disconnect fittings, which minimize any potential for leaks to occur during off-loading. The customers, who utilize the CAC, also have vapor recovery systems in place. The storage tank is vented to either a scrubber or back to the bulk container. To ensure a clean disconnect of the line, procedures are in place to purge the unloading line clear of product.

Our off-site customers are very experience in the handling of this material as evidenced by our on-site customer audits. These audits, conducted by our product steward, are required by our Global Product Stewardship Plan to be conducted at least every three years. Dow only approves customers who agree to specific storage and handling recommendations as well as on-site audits.

b. Environmental Fate

The potential for environmental exposure to CAC is negligible. There are minimal releases to the air, which occur through both point source and fugitive releases, but these represent only a fraction (<500 lbs.) of the CAC produced. There have been and should not be any releases to water or land unless a major plant upset occurred. In case of a plant upset or storage tank leak, CAC would be contained in the dike that surrounds the manufacturing and storage area

Since the CAC is consumed entirely as an intermediate, the downstream processing/use will result in yet a smaller fraction of air emissions than described above during manufacturing. As the residual level of CAC in downstream products is typically non-detectable (L.O.D. – 1ppm) and the downstream products are converted into other products, there is essentially no potential for environmental exposure through its use.

c. Human Exposure

The potential for human exposure is also extremely low. The total number of workers within our facility and our customers is less than 30 as the plants producing and processing these materials are small. Due to the very corrosive nature of CAC, personal protective equipment is worn during production, maintenance, distribution, and processing to ensure no personal contact. During normal operation this would include goggles and hard hats. During an operation, such as a line opening, where there is potential for residual CAC to be present, the protective equipment would include goggles, face shield, hard hat, protective full rubber suit, boots and a full-face respirator. Suitable positive-pressure self-contained breathing apparatus would be used for longer-term exposure in emergency situations such as a spill clean up.

Available monitoring data from the production of CAC, which is conducted periodically, indicates that the exposures are well below the industrial hygiene guideline established for CAC. The 8-hour Time-Weighted Average exposure limit for CAC, established by the American Council of Government Industrial Hygienists (ACGIH), is 0.01ppm, Skin, with an Excursion Exposure Limit of 0.05ppm, Skin. A summary of the actual monitoring data, from the activities, which are expected to have the greatest potential for worker exposures, is included in the table on the following page. During these activities, personal protective equipment is worn.

RESULTS FROM CAC INDUSTRIAL HYGIENE MONITORING

ACTIVITY	MONITORING DATA	SAMPLE DURATION	COMMENT
Connecting Loading Hose to CAC Isocontainer	0.005	11 min.	Personal Sample
Disconnecting Loading Hose from CAC Isocontainer	0.03 ppm	15 min.	Personal Sample
Disconnecting Loading Hose from CAC Isocontainer	0.01 ppm	15 min.	Personal Sample

As the residual level of CAC in downstream products is non-detectable (L.O.D. – 1ppm) and the downstream products are converted into other products, there is essentially no potential for worker or public exposure. The only potential for public exposure would be as a result of a significant manufacturing plant upset or transportation incident. We have a program in place to conduct root cause investigations if any such incidents were to occur and to develop a corrective action plan to prevent reoccurrence.

3. Conclusion

The Dow Chemical Company believes that the information above fully satisfies the EPA's criteria for closed-system intermediates. Further, the above information suggests that there appears to be little additional action that could be taken to prevent any further exposure, as the potential exposure opportunity is extremely limited.

B. Human Health Effects

There are six mammalian toxicity endpoints in the HPV Program (Results summarized in table on Page 8):

- Acute Toxicity
- Repeated Dose Toxicity
- Genetic Toxicity *In Vitro*
- Genetic Toxicity *In Vivo*
- Reproductive Toxicity
- Developmental Toxicity

Published and unpublished data, as detailed in the attached Robust Summaries, satisfy the requirements of Acute, Repeated Dose, and *In Vitro* Genetic Toxicity endpoints. Since in vitro genetic toxicity endpoints are negative, in vivo testing is not required. As CAC satisfies the EPA's criteria as a closed-system intermediate, the only data gap that exists is for a

Developmental Toxicity study. We are not proposing to conduct this study because we believe the corrosive nature of CAC would not allow us to conduct a study at a level that would result in any meaningful results. Further, when you consider the product stewardship precautions that are taken by Dow and our customers to minimize exposure, we don't believe that results from a developmental toxicity study would impact our handling recommendations.

The attached Robust Summaries provide adequate data to characterize the human health effects endpoints under the Program.

C. Ecotoxicity

(Results are summarized in a table on Page 8.)

There are three aquatic toxicity endpoints in the HPV Program:

- Acute Toxicity to Fish
- Acute Toxicity to Aquatic Invertebrates
- Toxicity to Algae (Growth Inhibition)

Published and unpublished data for chloroacetic acid, as detailed in the attached Robust Summaries, satisfies requirements for Acute Toxicity to Fish, Aquatic Invertebrates and Toxicity to Algae.

D. Environmental Fate

(Results are summarized in a table on Page 8.)

Predictive models were used to develop meaningful data for chemicals that are gaseous at relevant environmental temperatures and pressures. The environmental fate data includes:

- Photodegradation
- Stability in Water (Hydrolysis)
- Transport and Distribution (Fugacity)
- Biodegradation

1. Photodegradation

Photodegradation was estimated using models accepted by the EPA [2]. The computer program AOPWIN (atmospheric oxidation program for Microsoft Windows) [1] is used by The Dow Chemical Company. This program calculates a chemical half-life based on an overall OH reaction rate constant, a 12-hr day, and a given OH concentration. This calculation was performed for chloroacetyl chloride, as detailed in the attached Robust Summaries.

2. Stability in Water (Hydrolysis Testing and Modeling)

Chemicals that have a potential to hydrolyze include alkyl halides, amides, carbamates, carboxylic acid esters and lactones, epoxides, phosphate esters, and sulfonic acid esters [3]. Stability in water can be estimated using models accepted by the EPA [2]. This value has been calculated for chloroacetyl chloride, as detailed in the attached Robust Summaries.

3. Chemical Transport and Distribution In The Environment (Fugacity Modeling)

Chloroacetyl chloride is one compound in the series of chlorinated acetyl chlorides. These are acetyl chloride, chloroacetyl chloride, dichloroacetyl chloride, and trichloroacetyl chloride. Chloroacetyl chloride displays reactivity with water that is intermediate between acetyl chloride and dichloroacetyl chloride. Acid chlorides react with water to produce the corresponding carboxylic acid, hydrogen ion, and chloride. The generic reaction of acid chlorides and nucleophiles such as water, alcohols, and amines, is used for the laboratory scale preparation of the corresponding acids, esters, and amides and is referred to as an acylation reaction. These reactions proceed exothermically and generally occur rapidly at room temperature.

Chloroacetyl chloride decomposes rapidly and exothermically upon addition to water. An ampoule containing 3 g of CAC reacted completely in 750 mL of water in two hours, which corresponds to a $t_{1/2} < 30$ minutes. The authors note that the rate of reaction was limited by the rate at which CAC went into solution. When CAC is added in a co-solvent (in 150 mL of acetone) to 600 mL of water the reactions proceeded even more rapidly. In the gas phase, hydrolysis of chloroacetyl chloride and water vapor is slow.

Chloroacetyl chloride is highly reactive in water. Thus, the use of a partitioning model such as the multimedia fugacity model (EQulibrium Concentration model, or EQC) to determine its distribution among air, water, and soil does not yield meaningful results. Both Mackay Level I and Level III models were used to assess the fate and transport of CAC in the environment. These models use an equilibrium partition constant to scale or calculate mass transfer between two phases, where the constant is defined as the ratio of the equilibrium concentration in the two phases. A chemical, such as CAC, that reacts rapidly in one phase (water) doesn't have a definable concentration in that phase. Therefore a partition constant or mass transfer coefficient that includes the reactive phase can not be defined. Since these models require calculation of a partition constant between the various environmental compartments, they will provide flawed predictions for the fate and transport of highly reactive compounds such as CAC.

4. Biodegradation Testing

Little is known about the biodegradation of CAC in groundwater or soil. However, since this compound rapidly hydrolyzes in water, study of the biodegradation of CAC would have limited relevance to the environment. The major hydrolysis product, chloroacetic acid, has been well studied and passed the "readily biodegradable" 28-day test. Therefore, we suggest that biodegradability of CAC need not be measured in the laboratory. Rather, supplying information/references on the biodegradation of chloroacetic acid in groundwater will provide insight into the fate of CAC in the environment.

Biodegradation values for chloroacetic acid, as detailed in the attached Robust Summaries, were experimentally determined using OECD Guideline 302B, and used for choroacetyl chloride.

E. Physicochemical Properties

(Results are summarized in the "Description of the Chemical" on page 1.)

The physicochemical properties include:

- Melting Point
- Boiling Point
- Vapor Pressure
- Octanol/Water Partition Coefficient

Data for physicochemical properties will be summarized from various resources and detailed in the attached Robust Summaries.

IV. TEST PLAN SUMMARY

For reasons indicated in the above paragraphs, we do not believe additional data needs to be generated. Due to the manner in which the chemical is manufactured, distributed, and processed; the product stewardship measures taken to prevent exposure; and existing human/environmental data; we believe that our workers, the public and the environment are well protected from exposure to CAC. Additionally, due to the corrosivity of this compound, we do not believe that we could conduct a developmental toxicity study at levels that would produce any meaningful results. Finally, we do not believe that generation of any additional toxicity data will impact our product stewardship practices.

Test Plan for Chloroacetyl Chloride

Endpoint	Data Availability	Acceptable (Reliability)	Planned Testing
Acute Toxicity	LD50 = 207 mg/kg (rat) LC50 = 660 pm (rat) LC50 = 2400 ppm (mouse)	Acceptable (1)	None
Repeated Dose Toxicity	LOAEL = 0.5ppm (rats, mice, hamsters); inhalation 5d/wk for 4 weeks	Acceptable (2)	None
Genetic Toxicity *In Vitro*	Ames: Negative	Acceptable (2)	None
Genetic Toxicity *In Vivo*	Not available	Not necessary	None
Reproductive Toxicity	Not available	Not required	None
Developmental Toxicity	Not available	Not necessary	None
Acute Toxicity to Fish	CAC: LC50 = 369 mg/L (Lebistes reticulatus)	Acceptable (2)	None
Acute Toxicity to Aquatic Invertebrates	EC50 = 22-75 mg/L (Daphnia magna)	Acceptable (2)	None
Toxicity to Algae (Growth Inhibition)	CAC: EC50 = 0.028 mg/L (Scenedesmus subspicatus)	Acceptable (2)	None
Photodegradation	Halflife = 450 days (calculated)	Acceptable (2)	None
Stability in Water (Hydrolysis)	Halflife (pH 7) < 30 minutes at 25 deg. Centrigrade (calculated)	Acceptable (2)	None
Transport and Distribution (Fugacity)	Model does not produce meaningful distribution values due to reactivity in water.	Acceptable	None
Biodegradation	100% after 28 days	Acceptable (2)	None

REFERENCES

1. EPIWIN. 1999. Estimation Program Interface for Windows, version 3.02. Syracuse Research Corporation, Syracuse, NY, USA.
2. US EPA. 1999. Determining the Adequacy of Existing Data. OPPT, EPA.
3. Neely, W. B. 1985. Hydrolysis. In: W. B. Neely and G. E. Blau, eds. Environmental Exposure from Chemicals. Vol I., pp. 157-173. CRC Press, Boca Raton, FL, USA.